# LUMINESCENT CHARACTERISTICS OF BENZOXAZOLINONE AND ITS PROTOTROPIC SPECIES

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### Summary

The absorption and fluorescence characteristics of benzoxazolinone, *N*-methylbenzoxazolinone, 2-ethoxybenzoxazole and 5-chlorobenzoxazolinone have been recorded in different solvents and at various acid concentrations. Using the Pople-Pariser-Parr and complete neglect of double overlap integral/spectroscopy-CI semi-empirical methods, the excited states of the keto and enol forms and their various prototropic species have been analysed. The above studies have clearly established that the lowest energy transition is of  $\pi \rightarrow \pi^*$  in character and the keto form is present in all solvents. Both the band systems arise from the benzene ring and are perturbed by the >NH and -O-C groups, ortho to each other. The monocation is formed by protonation of the carbonyl group and the monoanion is formed by deprotonation of the enolic proton. The lowest energy transition is charge transfer in character for the monocation and of  $\pi \rightarrow \pi^*$  for the monoanion.

## **1. Introduction**

Whenever a labile hydrogen atom is present at ortho or para position to the carbonyl group, there is keto-enol tautomerism [1]. Stability of the respective tautomer depends upon the nature of the compound, and on the nature of the environment. For example, 2-hydroxybenzimidazole [2], mainly exists as 2-(3H)-benzimidazolone in all the solvents. Even alkylation and arylation leads to N-substituted derivatives rather than to O-substituted ones [3]. However, protonation and deprotonation lead to the structural organization and the respective ions have benzimidazole structure [2]. In addition, 3-hydroxyindazole exists in the enol form in nonpolar solvents and in the keto form (3-indazolinone) in polar solvents [4]. In polar solvents, the fluorescence is observed from both forms. Behaviour of the prototropic species of 3-hydroxyindazole conform to the indazole structure.

A preliminary study by Morales *et al.* [5] has indicated that 2-hydroxybenzoxazole (B-OH) exists mainly in the keto form as 2-benzoxazolinone

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(Bn), both in the ground and first excited singlet states and in different solvents. The aims of the present study on this molecule are as follows: (i) to investigate the spectral characteristics and the structure of the different prototropic species; (ii) to observe the effect of the chlorine atom on the spectral aspects of the various species of Bn; (iii) to determine the  $pK_a$  values of these prototropic reactions in  $S_0$  and  $S_1$  states. Semi-empirical calculations (both PPP and CNDO/S) have been carried out to establish the nature of transitions, oscillator strengths and structural aspects of the various prototropic species of Bn. A similar study was carried out on *N*-methylbenzoxazolinone (NMBn) and 2-ethoxybenzoxazole (EBO) to substantiate the above results.

## 2. Experimental details

Bn and 5-chlorobenzoxazolinone (CBn) were procured from Aldrich Chemical Company. NMBn [6] and EBO [7] were prepared as suggested in the literature. The compounds were purified by repeated recrystallization and the purity was checked by TLC, melting or boiling points and by recording the fluorescence excitation spectrum (which matches with the corresponding absorption spectrum). Solvent purification and experimental methods were as already reported in earlier papers [8-10]. The concentration of the solutions was approximately  $10^{-4}$  M.

## 3. Results and discussion

The absorption and fluorescence spectra of Bn, CBn, NMBn and EBO were recorded in five different solvents and in the acidic/basic range from  $H_0$  –10 to  $H_-$  16. The relevant data are compiled in Table 1. The spectral data of Bn match well with data reported by Morales *et al.* [5].

Theoretical as well as spectroscopic data have already established for benzoxazole (BO) that the long wavelength band (long axis polarized) is localized on the benzene ring and the short wavelength (short axis polarized) band is on the oxazole ring [11 - 14]. The Bn molecule can have two forms: enol (III) and keto (III'). For the enol form, the short wavelength band (231 nm) would have been more perturbed and red shifted than the long wavelength (276 nm) band. Our data show the opposite behaviour (*i.e.* red shift in the 276 nm band and blue shift in the 231 nm band) and thus it can be concluded that the Bn molecule exists in the keto form, agreeing with the earlier results [5]. Results of EBO show that the absorption spectrum of BO is not affected by the presence of the ethoxy group at position 2, indicating that the inductive effect of the ethoxy group is more predominant than the resonance effect [16]. Similar results have been observed earlier [5]. The keto form of Bn can be approximated to two parts: one a benzene molecule with amino (>NH) and ether (-O-C) groups at ortho positions, and the second a

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Absorption	solvents and

Solvent/species	Bn		NMBn		EBO		CBn	
	$\lambda_{\max}(abs)$	$\lambda_{\max}(flu)$	$\lambda_{\max}(abs)$	$\lambda_{\max}(flu)$	$\lambda_{\max}(abs)$	$\lambda_{\max}(flu)$	$\lambda_{\max}(abs)$	$\lambda_{\max(f u)}$
Cyclohexane	281 (3.62)	295 (0.12)	285 (3.73)	295 (0.1)	277	295	284 (3 71)	310
	275 275 (3.7) 226 (3.85)		278 278 (3.69) 273 (3.78)		271		(11.0)	
Dioxane	281 (sh)	295 (0 13)	280 (sh)	295 20 00)	277	295	284	312
	(3.45) 276 (3.45) 228 (3.61)	(21.2)	(au) 277 (3.92)	(60.0)	271			
Acetonitrile	278	295 295	280	295 202	276	293	282	310
	(su) 274 (3.67) 226 (3.86)	(71.0)	(sn) 275 (3.95)	(on.n)	270		(3.73)	
Methanol	277 (sh)	295 (0.09)	276 (sh)	295 (0.06)	276	290	282	310
	273 273 226 (3.97)		(3.72) (3.72)		269		(01.0)	

(continued)

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Solvent/species	Bn		NMBn		EBO		CBn	
-	$\lambda_{\max}(abs)$	$\lambda_{max}(flu)$	$\lambda_{\max}(abs)$	$\lambda_{\max(flu)}$	λ <sub>max</sub> (abs)	$\lambda_{\max}(flu)$	$\lambda_{\max}(abs)$	$\lambda_{\max}(flu)$
Water DH = 6.3	277 (sh)	295 (0.04)	276 (sh)	295 (0.02)	275	290	279 (4.14)	310
4	271		272		269			
	(3.69)		(3.67)					
	223 (3.95)							
Monocation	269	I	270		ł	1	280	1
$H_0 = -9$	(3.62)		(3.6)				272	
	220		264				267	
	(3.92)		(3.62)				(us)	
Monoanion	279	1	i	I	1		ì	i
pH = 13	(3.78)							
	238							

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TABLE 1 (continued)

 $\stackrel{\rm N}{\Omega}>C=O$  molecule joined to the benzene ring. The effect of these substituents on 257 nm and 200 nm bands, originating from the benzene ring, can be calculated using relations given by Stevenson [17]. These absorption maxima should be at about 280 nm and 233 nm, which agree well with the experimental results. The results of NMBn further substantiate this conclusion as the >NCH<sub>3</sub> group is more electron-donating than the -NH<sub>2</sub> group, and both the band systems are red shifted. The absorption spectrum of CBn is consistent with the above explanation, as the chlorine atom is present on the benzene ring and will thus perturb the transitions originating predominantly from the benzene ring. The short wavelength band system could also be due to the  $n \rightarrow \pi^*$  transition of the carbonyl group which has a similar location to that in the carbonyl group, perturbed by amino and ether groups. However, this band system could have occurred at about 210 nm with a much lower extinction coefficient [18]. This indicates that the Bn molecule exists as the keto form and both the band systems are localized on the benzene ring.

The effect of solvents on the absorption spectrum is consistent with the above mentioned arguments *i.e.* hydrogen bonding may be occurring at the lone pair of >N-H group causing a blue shift. Although no change is observed in the fluorescence band maximum, the decrease in the fluorescence quantum yield can be associated with the interaction of hydrogen bonding solvents with the solute.

The species formed at high base  $(pH \ge 9)$  and high acid concentrations  $(H_0 \le -2)$  are the monoanion and the monocation of Bn and CBn respectively. Behaviour of NMBn is similar to that of Bn in the  $H_0/pH$  range of -10 to 9, but are hydrolysed at pH > 9, whereas EBO decomposes in highly acidic and basic conditions. Both these ionic species are nonfluorescent at room temperature. The  $pK_a$  values in the ground state were determined using absorption spectral data and  $pK_a^*$  values by fluorimetric titrations. The Forster cycle method cannot be used because either the species are nonfluorescent or some structural changes take place.

The spectral data (a small red shift in the 277 nm and a large red shift in the 231 nm bands of BO) as well as the  $pK_a$  value (9.2) for the neutralmonoanion equilibrium indicate that Bn(III') transforms first to the enol form (III) and is then deprotonated. This is further confirmed by the appearance of a 238 nm band of BO, which is absent in the keto form of Bn. The low  $pK_a$  value (8.7) for the similar equilibrium of CBn indicates that the inductive effect of the chlorine atom is more predominant than the resonance effect. This result is different from the deprotonation of benzimidazolone [2], but similar to that of indazolinone [4]. However, monocation is formed by the protonation of the keto group (III'). Had the molecule been in the enol form (III), the  $pK_a$  for the monocation-neutral equilibrium would have been slightly greater than that of BO [19] (-0.1) because of the presence of an electron-donating hydroxyl group. Our results indicate that the  $pK_a$  value for this equilibrium (-4.7) is closer to that of the protonation reaction of the keto group [20]. Furthermore, reorganization of the charges

Molecule	Monocation-	-neutral	Neutral-	monoanion	
	рК <sub>а</sub>	pK <sub>a</sub> *	pKa	pK <sub>a</sub> *	
Bn	-4.7	-1.8	9.2		
CBn	~-5.0		8.7	_	
NMBn	-5.0	-2.1	_		

Dissociation constants of the various prototropic reactions of Bn, CBn and NMBn in the ground and first excited singlet states

in (II) to form (I) cannot be ascertained from our results. Though the pK<sub>a</sub> value for the similar reaction of CBn cannot be determined accurately (because of very small spectral changes occurring in the formation of the monocation), it is nearly equal to -4.7 and thus a similar explanation can be offered as given for the monocation-neutral equilibrium of Bn. As with the prototropic reactions of benzimidazolinone, both the ionic species of Bn and CBn are non-fluorescent. The data in Table 2 are consistent with the fact that the carbonyl group becomes more basic in the  $S_1$  state and also confirm that  $\pi \rightarrow \pi^*$  is the lowest energy transition. However, the neutral-monoanion equilibrium is not established in  $S_1$  state, indicating that the rates of radiative transitions are greater than the rates of deprotonation/protonation reactions. Non-fluorescent monoanions and ground state pKa values are also observed from the fluorimetric titration of phenols [21]. The prototropic behaviour of NMBn is similar to that of Bn in the acidic range and can be explained along the same lines. The various prototropic reactions of Bn are depicted in Scheme 1.



Scheme 1.

TABLE 2

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Electronic transitions, oscillator strength, transition moment polarization angle ( $\alpha$ ) and charge densities at various basic centres in S<sub>0</sub> and S<sub>1</sub> states (PPP method)

Singlet transition.	s ( <b>λ</b> , nm)	Oscillation	Polarization	Charge De	nsities	-		Dipole mor	nent (D)
Experimental	Theoretical	strength (f)	α <sup>(</sup> °)	$N_3$	0 <sub>10</sub>	N <del>3</del>	0 <sup>*</sup> 0	ц	*π
Bn									
281	285	0.0417	134	1.7306	1.5085	1.641	1.473	3.02	1.2207
275	243	0.4399	188						
226	216	0.6351	152						
B-OH									
	286.6	0.0421	167	1.3509	1.8918	1.349	1.885	3.579	3.413
	264	0.5272	301						
	225	0.2733	33						
	209	0.0496	259						
NMBn									
285	287.9	0.0525	125	1.717	1.9918	1.612	1.979	3.068	1.134
278	253.0	0.4673	199						
231	217.6	0.51178	166						
	208.7	0.4343	343						

 $\alpha$  = is angle measured counter-clockwise to z-axis.

## 3.1. Quantum-mechanical calculations

Both PPP and CNDO/S-CI computational methods [22 - 28] were used to study the ground and excited state structures of the molecules in different prototropic forms. In CNDO/S-CI, the first 40 monoexcited configurations were taken into account in the CI procedure. The experimental parameters were those of Del-Ben and Jaffe [24] and the molecular structure was considered planar with standard geometrical parameters (Fig. 1).

PPP calculations were carried out only on the keto and enol forms of the neutral species (Table 3) because the parameters for the monocation and monoanion were not available, whereas CNDO/S calculations have been performed for all three species (monocation, neutral and monoanion), both in their keto and enol forms. The experimental and calculated transition wavelengths of different prototropic species of Bn, together with their oscillator strengths and the direction of the transition moment, are compiled in Table 4. The results obtained for the keto form agree with those of Morales et al. [5], as well as with the experimental values, with the difference in the values of the dipole moment in the  $S_0$  and  $S_1$  states. Although it is difficult to predict from PPP data whether the keto form is more favourable. the data in Table 4 show that the Bn molecule cannot exist in the enol form because the agreement with the experimental results is not good. Furthermore, the hydroxyl group is an electron-donating group and presumably the direction of the transition moment should be away from this group. The data in Table 4 show that for the enol form the direction of the transition moment for the first three transitions is towards the hydroxyl group, whereas for the fourth one it is at  $80^{\circ}$  to the z-axis. However, for the keto form both of the transition moments are polarized towards the benzene ring.

The contributions of the various molecular orbitals involved in the longest wavelength singlet transitions and their localizations at various atomic centres are listed in Table 5. It can be seen that (although not all of the homos are rigorously localized on the benzene ring) most of the homos are localized on the benzene ring. For the keto form lumo, involved in both of the transitions, is localized mainly on the benzene ring, but this is not true for the enol form. This confirms the earlier conclusion that the long wavelength band originates from the benzene ring and also that Bn exists in the keto form. In the case of the monocation, the lumo is localized on the oxazole ring indicating that charge migration takes place from the benzene ring to the heterocyclic ring. The driving force behind this charge migration is the presence of a positive charge on the heterocyclic ring, agreeing with the earlier observation that the lowest energy transition in the monocation of benzoxazole is a charge transfer. Based on earlier results, the monoanion is in the enol form and lumo is localized on the benzene ring. The presence of a negative charge could hinder the flow of charge from the homo to the heteronuclear system.

The electron densities at different basic centres for the ground and first excited singlet states for different prototropic species of the keto and enol form of Bn are compiled in Table 6. The data in Table 6 indicate that in

**TABLE 4** 

Electronic spectra of Bn and B-OH and their various prototropic species

<b>Amax</b>	Amax	Keto form			λmax	Enol form			
(expt)	(CNDO/S)	Oscillator strength	κ°	Type	(calc)	Oscillator strength	σ	Type	
Neutral sp	ecies								
281	283	0.015	176	א⊐ <b>+</b> =	289	0.02	348	$\pi \rightarrow \pi^*$	
275	279	0.00	64	<b>ב → ב</b> *	262	0.24	352	$\pi \rightarrow \pi^*$	
226	238	0.067	245	π → π*	251	0.002	344	π → π <b>*</b>	
1	I	Ι	ł		225	0.09	50.4	$\pi \rightarrow \pi^*$	
Monocatic	u								
269	304	0.121	175	<i>ד</i> → <i>π</i> *	320	0.142	353	$\pi \rightarrow \pi^*$	
223	275	0.007	106	א → ח <b>*</b>	311	0.018	60	$\pi \rightarrow \pi^*$	
220	268	0.02	196	$\pi \rightarrow \pi^*$	265	0.031	20	<i>ו</i> → ה <b>*</b>	
Monoanio	u								
ĺ	334	0.07	143	א → ד <b>*</b>	330	0.082	332	$\pi \rightarrow \pi^*$	
279	291	0.247	201	* → ۲*	298	0.257	76	$\pi \rightarrow \pi^*$	
238	217	0.067	<b>8</b> 6	א → ד <b>*</b>	230	0.128	172	$\pi \rightarrow \pi^*$	

Keto Form					Enol Form				
Transition	Configuration	% Contribution	M.O. (Type)	Localization	Transition	Configuration	% Contribution	M.O. (Type)	Localization
Neutral Sp	ecies								
•			21 o	Delocalised					
283	25  ightarrow 26	93.2	25 π	1,3,5,6,8,9,1(	) 289	25  ightarrow 26	20.0	<b>25</b> π	2, 3, 4, 6, 8, 9
			28 π	1,2,3,10		25  ightarrow 27	71.0	26 π	2,3,4,6,7
279	23  ightarrow 28	64.28	$23 \eta$	1,10				27 π	4,5,7,8
	$24 \rightarrow 27$	17.2	26 π	4, 5, 6, 7, 8, 9	262	25  o 26	36.8	23 o	delocalized
	$21 \rightarrow 27$	11.6	27 π	5,6,8,9		25  ightarrow 27	19.9	25 π	2, 3, 4, 6, 8, 9
						25   28	11.2	26 π	2, 3, 4, 6, 7
						23  ightarrow 26	14.3	27 π	4,5,7,8
						23  ightarrow 28	15.3	28 π	2,3,6,7,9
Monocatio	u								
304	25  ightarrow 26	93.3	$24 \pi$	4,5,6,7,8	320	25  o 26	95	23 J	delocalized
	25  ightarrow 28	4.3	25 π	2, 3, 5, 6, 8, 9	311	24  ightarrow 26	96	24 π	4,5,7,8
275	24  ightarrow 26	82.7	$26 \pi$	1, 2, 3, 10	265	24  ightarrow 27	47.4	25 π	2,3,5,6,8,9
	25  ightarrow 28	13.3	28 π	4, 5, 6, 7, 8		24  o 28	39.5	26 π	1, 2, 3, 10
						$23 \rightarrow 27$	8.0	27 π	5,6,8,9
								28 π	4, 5, 6, 7, 8, 9
Monoanior	1								
334	$24 \rightarrow 28$	8.6	23 o, n	1, 2, 3, 10	330	24  ightarrow 26	8.6	19 σ	delocalized
	24  ightarrow 26	9.7	24 π	1, 3, 4, 5, 7, 8		24  o 28	9.7	$24 \eta$	1, 3, 10
	25  ightarrow 26	89.3	25 π	3, 4, 6, 8, 10		$25 \rightarrow 26$	80.3	25 π	3, 4, 6, 8, 10
291	$23 \rightarrow 27$	6.6	27 π	5,6,7,8,9	230	$19 \rightarrow 26$	11.1	26 π	2, 3, 5, 7, 8, 9
	$25 \rightarrow 27$	87.1	28 π	5,6,7,8,9		$24 \rightarrow 27$	7.6	27 π	2,5,6,8,9
				•		25  ightarrow 28	78.2	28 π	1, 2, 3, 6, 7, 10

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Contribution of various molecular orbitals involved in the longest wavelength singlet transition and their localizations

**TABLE 5** 

#### TABLE 6

Species	Atomic	Keto form	l	Enol form	
	centre	Ground	Excited	Ground	Excited
Neutral	01	6.138	5.805	6.092	6.055
Neutral Monocation Monoanion	N 3	5.153	5.308	5.220	5.333
	O 10	6.390	6.468	6.192	5.783
Neutral Monocation Monoanion	01	6.046	6.007	6.013	6.073
	N 3	5.045	5.000	5.006	5.106
	O 10	6.034	6.057	6.123	6.097
Monocation Monoanion	01	6.156	6.162	6.140	6.144
	N 3	5.403	5.734	5.419	5.681
	O 10	6.485	6.598	6.645	6.997

Electron densities at various centres of Bn and its prototropic forms in the ground and first excited states

both the keto and enol forms the charge density at the tertiary nitrogen atom increases in the  $S_1$  state, whereas it increases at the oxygen atom of the keto group and decreases at the oxygen centre of the enol form. These results are consistent with experimental findings that the tertiary nitrogen atom and carbonyl group become more basic, whereas the hydroxyl group is more acidic on excitation.

Charge density calculations on the monocation or the monoanion do not shed any light on the structure of the species. For example for the monocation formed by the protonation of the keto group, the charge density will decrease on the tertiary nitrogen atom because the presence of a positive charge on the carbonyl group withdraws the charge from nearby atoms; also, it becomes more basic on excitation. A similar explanation can be given for the monocation of the enol form.

## 4. Conclusions

The following conclusions can be drawn from this study. (i) Bn exists as the keto form both in the  $S_0$  and  $S_1$  states in all the solvents, and methylation takes place at >N rather than at -O. (ii) Both the band systems originate from the benzene ring and are perturbed by the presence of >NH and -O-C groups ortho to each other. (iii) Protonation takes place at the carbonyl oxygen and deprotonation from the enolic proton. (iv) The monocation and monoanion are non-fluorescent at room temperature. (v) The above assignments of transitions in the various prototropic forms are confirmed by the semi-empirical PPP and CNDO/S-CI calculations.

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